Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.


**Supplemental Material**

| Uranium and Am isotope ratios for spiked geostandard samples. | | | | |
|---|---|---|---|---|
| | $^{234}U/^{238}U$ | $^{235}U/^{238}U$ | $^{236}U/^{238}U$ | $^{241}Am/^{243}Am$ |
| BCR-2A | 0.0171(1) | 1.738(2) | 0.0264(2) | 0.653(2) |
| BCR-2B | 0.0149(1) | 1.517(2) | 0.0230(2) | 0.640(2) |
| BCR-2C | 0.0098(1) | 0.997(2) | 0.0151(2) | 0.606(2) |
| BCR-2D | 0.0175(1) | 1.771(2) | 0.0269(2) | 0.647(2) |
| BHVO2+ | 0.01043(2) | 1.0003(1) | 0.00152(1) | - |

| Plutonium isotope ratios for spiked geostandard samples. | | | | |
|---|---|---|---|---|
| Sample | $^{238}Pu/^{239}Pu$ | $^{240}Pu/^{239}Pu$ | $^{241}Pu/^{239}Pu$ | $^{242}Pu/^{239}Pu$ |
| BCR-2x | 0.00263(8) | 0.2407(3) | 0.00525(8) | 0.01561(5) |

Background-corrected isotope ratios were calculated according to:

$$R_{ab} = \frac{(N_a - N_{a,B})}{(N_b - N_{b,B})} \quad (1)$$

where $N_i$ is the number of counts in peak $i$ and $N_{iB}$ is the number of background counts in peak $i$.

The uncertainty in isotope ratio measurements is calculated from counting statistics:

$$\sigma^2 = \sum_i \left(\frac{\delta R_{ab}}{\delta N_i}\right)^2 \sigma_i^2 \quad (2)$$

where $\sigma_i$ is the uncertainty in $N_i$. Applying (2) to (1) and recognizing that for counting statistics $\sigma_i = \sqrt{N_i}$ gives:

$$\sigma^2 = \frac{N_a}{(N_b - N_{b,B})^2} + \frac{N_{a,B}}{(N_b - N_{b,B})^2} + \frac{N_b (N_a - N_{a,B})^2}{(N_b - N_{b,B})^4} + \frac{N_{b,B}(N_a - N_{a,B})}{(N_b - N_{b,B})^4} \quad (3)$$

which, after simplification, yields

$$\sigma = R_{ab} \sqrt{\frac{N_a + N_{a,B}}{(N_a - N_{a,B})^2} + \frac{N_b + N_{b,B}}{(N_b - N_{b,B})^2}} \quad (4)$$